Germanium Bond Refractions

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The Lorentz-Lorenz molar refraction, R_D, was calculated for a large number of organogermanium compounds, using literature data for density and refractive index (D-line, 20°). On the assumption of the additivity of bond and structural refractivities, the commonly accepted data for such measurements were employed for the calculation of refraction values for germanium-containing bonds. Equations of the type, $R_D = a \cdot n + b$, where n is the number of carbon atoms in a single alkyl group, were derived for 20 different classes of organogermanium compounds. The equations have a reproducibility of better than one per cent.

VALUES FOR THE refraction of bonds involving germanium were summarized by Vogel and coworkers (*6*). The results of that study were based on 36 representative compounds, and many of the calculated Lorentz-Lorenz molar refractions, R_D, (D-line), and subsequent bond values were reported to only one decimal. Furthermore, R_D was evaluated at various temperatures (although the temperature coefficient of R_D is approximately 1 % per 5°, such a variation could affect the final bond values to a certain extent).

The appearance of a recent review article on organogermanium compounds (*4*) prompted a more comprehensive investigation of the refraction of germanium-containing bonds. R_D was calculated in the usual manner from literature values for density and refractive index (D-line, 20°) (*4*), and, on the assumption of the additivity of bond and structural refractivities, the commonly accepted data for such measurements (*5*) were employed for the calculation of the bond values of interest. The results of these calculations are presented in Table I, along with previous findings (the figures in brackets are the number of representative compounds used by the other workers).

Table I. Germanium Bond Refractions (D-line, 20°)

Bond	Number of Compounds	Refraction Cc./Mole	Other Results
Ge-C_{alkyl}	65	3.00 ± 0.06	3.05 [6] (*6*)
Ge-C_{aryl}	3	4.76 ± 0.18	
Ge-F	4	2.22 ± 0.05	1.3 [2] (*6*)
Ge-Cl	37	8.00 ± 0.09	7.6 [4] (*6*)
Ge-Br	15	11.14 ± 0.13	11.1 [4] (*6*)
Ge-I	8	17.13 ± 0.16	16.7 [2] (*6*)
Ge-O	40	2.52 ± 0.09	2.47 [6] (*6*)
Ge-S	8	6.73 ± 0.16	7.02 [7] (*6*)
Ge-N	6	2.14 ± 0.11	2.33 [5] (*6*)
Ge-H	26	3.64 ± 0.04	3.34 [1] (*3*)
Ge-D	6	3.65 ± 0.08	
Ge-Ge	1	6.85	

Elements bonded to aromatic carbon show a greater refraction than when bonded to aliphatic carbon. Furthermore, the mobility of the π-electrons in aromatic systems precludes any high degree of reproducibility for the refraction of bonds to such systems (*2, 5*): thus, the large deviation in R(Ge-C_{aryl}), (Table I), is not unexpected. The rather large deviations indicated for R(Ge-O) and R(Ge-N) are in line with errors associated with small refraction values (the relatively small deviation in R(Ge-F) may be attributed to the selection of only four concordant values out of a total of eight calculated for this bond).

A linear relationship has been demonstrated between R_D and n, the number or carbon atoms in a single alkyl group, for numerous classes of organoboron compounds (*1, 2*). Table II lists values of the constant a and b, in the equation, $R_D = a\ n + b$, for 20 different classes of organogermanium compounds (*4*). Since R_D for various isomers are practically the same, average values were used in the derivations. The constants were evaluated by a least-squares calculation, and the resulting equations have a reproducibility of one per cent and better.

The constant a, divided by the number of alkyl groups in any given class of compounds, gives a measure of the refraction contribution of the methylene group, R_{CH_2}. The mean value of R_{CH_2} from the 20 classes listed in Table II, is 4.647 cc. per mole; this figure being in close accord with the accepted value for long series of homologs (*5*).

Table II. Constants for the Equation, $R_D = a\ n + b$

Class	*a* ; *b*	Class	*a* ; *b*
R_4Ge	18.65 ; 13.12	R_3GeNCS	13.96 ; 27.85
$(C_2H_5)_3GeR$	4.624 ; 41.24	$(RO)_4Ge^a$	18.67 ; 17.04
$RGeH_3$	4.612 ; 14.49	$C_2H_5Ge(OOCR)_3$	13.98 ; 39.13
R_2GeH_2	9.317 ; 13.84	$(i\text{-}C_3H_7)_2Ge(OOCR)_2$	9.505 ; 52.21
R_3GeH	13.90 ; 13.92	$(C_2H_5)_3GeOOCR$	4.655 ; 47.00
$RGeCl_3$	4.620 ; 27.45	$(i\text{-}C_3H_7)_3GeOOCR$	4.570 ; 61.24
R_2GeF_2	9.313 ; 11.19	$(C_2H_5)_3GeSR$	4.666 ; 49.53
R_2GeBr_2	9.428 ; 28.70	$CH_2{=}CHGeR_3$	13.97 ; 22.34
R_3GeCl	13.96 ; 17.91	$CH_2{=}CHCH_2GeR_3$	13.53 ; 27.93
R_3GeBr	13.99 ; 21.05		
R_3GeI	13.95 ; 27.28		

[a] at 25°

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Ternary Systems of Liquid Sulfur Dioxide

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This paper presents in a concise arrangement experimental graphs of 15 aqueous and 60 nonaqueous systems of liquid sulfur dioxide under pressure and usually at room temperature. They are ternary except the last five which have an extra component as a diluent. Most of the systems show two liquid phases. The graphs include the usual types and also some special features—such as isopycnics, iso-optics, solutropes, island curves, and separate binodal curves. Some of these graphs are pertinent to solvent extraction with mixtures including sulfur dioxide.

APPLICATION of liquid sulfur dioxide for solvent extraction of hydrocarbon oils was demonstrated over 50 years ago by Edeleanu (2). During that time, it has been one of the most widely used selective solvents for that purpose. Processes employing it have aided in development of chemical engineering for handling condensed gases of moderate pressure.

Advantages of sulfur dioxide over other selective solvents are low cost, convenient transfer owing to pressure, stability, relative inertness when anhydrous, and easy recovery. The chief limitation of sulfur dioxide is the extreme dependence of solubility on the molecular weights of the hydrocarbons. Those of the gasoline range have high solubility, and those of the lubricating oil range have low solubility. The selectivity of sulfur dioxide for type of hydrocarbon is sometimes masked by the effect of molecular weight. This is especially true for cycloparaffins over paraffins, in which the selectivity is negligible for comparable molecular weight.

Extensive studies of mutual solubilities of sulfur dioxide and hydrocarbons have been made by Seyer and coworkers as cited by Francis (3). The apices of their binary graphs are critical solution temperatures (CST), which summarize the studies. CST of sulfur dioxide have been published also by Leslie (*17*), and by others. Such temperatures are listed (*4*) for 50 hydrocarbons and for 40 nonhydrocarbons.

The CST of sulfur dioxide and water were observed by Terres and Rühl (*21*) as 133°, and by Spall (*20*) as 128°. An early unpublished observation of the present author (1932) had agreed with Terres, and also noted an isopycnic at 129.5° (temperature of equal densities of the layers). Butcher and Hanson (*1*) observed mutual solubilities up to 65°.

The solubility of liquid sulfur dioxide in water, 26%, is much greater than that of water in liquid sulfur dioxide, 1.5%. This is characteristic of many pairs of liquefied gases with less volatile components (*9*). Solubility of sulfur dioxide at low pressures is available (*16, 19*) in aqueous and many other solutions.

Although solvent extraction typically involves a ternary system, only a few such systems with sulfur dioxide have been published. Satterfield and coworkers (*18*) presented eight ternary systems with liquid sulfur dioxide, an aromatic hydrocarbon, and a nonaromatic hydrocarbon (one combination at three temperatures). All were at low temperature, below the boiling point of sulfur dioxide, −10°, and so at atmospheric pressure. They are all graphs of the usual bite type. The only published graphs for systems of sulfur dioxide under pressure and two other pure components are those of propane with propylene (*12*) or with hydrogen cyanide (*11*); and those of carbon dioxide (*9*) with cetane, methylnaphthalene, or octadecane.

This paper presents 75 ternary sulfur dioxide systems (further data may be obtained from the author). These all involve a liquid phase rich in sulfur dioxide under pressure, and at room temperature unless otherwise indicated. Most of them show two liquid phases, although a few have as one component a fairly soluble solid such as urea; some of these show only a solid-liquid equilibrium (graphs 11, 19, 33, 35). The purpose of this research was to find combinations of solvents suitable for concentrating benzene or other aromatics or olefins from more saturated hydrocarbons.

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